THE SECONDARY K-ABSORPTION SPECTRA OF FERRIC OXIDE IN SOLID AND IN COLLOIDAL SOLUTION*

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ABSTRACT. Secondary K-absorption spectra of colloidal solution of ferric oxide have been investigated and compared with those obtained in solid ferric oxide. An extended secondary structure has also been found in the colloidal solution. A comparison of the secondary structure in the solid state of ferric oxide and in the state of colloidal solution has revealed that the positions of the succeeding maxima and minima are not identical in the two cases. Marked difference has also been noticed in the position and width of the primary edge. These results have given rise to important speculation as to the nature of the colloidal particles. From this experiment it has not been possible at the present moment to decide definitely whether these colloidal particles are simple molecular aggregation or crystallites of Fe_2O_3.

INTRODUCTION AND EXPERIMENT

The behaviour of substances in the colloidal state has been the subject of interesting and important study in physical chemistry. The colloidal particles, as we know, are matter in finest division having their diameter small enough to share the random motion of the molecules in accordance with the well-known gas kinetic laws and do not settle under the force of gravity, but are large enough compared to single molecules so as to be visible under ultra-microscope. The radii of the colloidal particles usually ranges from 10^{-5} to 10^{-7} cm.† Each particle is therefore formed of several molecules clustered together. Now each colloidal particle, say Fe_2O_3, may be crystalline, the oxygen and iron atoms being regularly arranged or it may be a cluster of several Fe_2O_3 molecules. We have undertaken this investigation with the view that the study of the secondary structure may throw some light on this question.

An electron type of metal X-ray tube was used for the present investigation. The slit of the spectrograph, which is adjustable, was kept constant at .1 mm. It

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† The Physical Properties of Colloidal Solution (3rd Edition), E. F. Burton.

was covered with a thin aluminium foil and the well-known Bragg focussing method was adopted. The dispersion on the photographic plate was 15.6 X.U. per mm. Each negative plate was microphotographed at several points for precision measurement and the dispersion on the microphotograph was 2.4 X.U. per mm.

The colloidal solution was prepared in the following way. Ferric hydrate $Fe(OH)_3$ precipitated from ferric chloride solution by adding ammonium hydroxide is filtered and well washed with distilled water to remove the trace of NH_4OH and Cl_2. The precipitated ferric hydroxide is then added to a saturated solution of ferric chloride and the whole was then well shaken. The colloidal solution of ferric oxide is thus obtained. On long standing, the coarse particles, formed at first, gradually break up into finer ones. One such colloidal solution having its particle size roughly of the order of 10^{-6} to 10^{-7} cm. in diameter has been investigated.

A special type of cell holder was designed for the purpose in which the colloidal solution may be contained and exposed to the path of X-ray beam. It consists of two rectangular brass plate in which similar rectangular slots were cut out. A thin piece of rubber sheet was placed between the plates and screwed at four corners. The solution is contained in the rectangular opening; the two surfaces of the plates were covered by thin pieces of celluloid film.

The results on colloidal ferric oxide as well as on solid ferric oxide are given in tables I and II. The position of the succeeding maxima and minima are given in X.U. The differences of the position of these maxima and minima from the main edge are given in X.U. and in electron volts.

The following peculiarities are noteworthy :

1. The secondary absorption edges appear on the short-wavelength side of the principal K-absorption edge of iron in colloidal solution of ferric oxide, and extend to about 200 volts from the main edge.

2. The distances of the secondary maxima and minima in volts from the principal absorption edge have not come out identical in colloidal Fe_2O_3 and in solid Fe_2O_3. The intensity distribution in the fine structure in the two cases is also different.

3. The position of the primary edge in colloidal solution has shifted to longer wavelength compared to that in the solid state.

4. The width of the edge has also increased in the colloidal solution.

TABLE I

Solid and Colloidal Ferric Oxide

		K	A	α	B	β	C	γ	D	δ	E	ε	F
Solid Fe_2O_3	λ in X.U.	1736 4	1732.8	1727.8	1722 1	1717.7	1714.0	1711.8	1703.5	1698.3	1694.7	1689.7	1687.3
	δλ	0	3.6	8.6	14.3	18.7	22.4	24.6	32.9	38.1	41.7	46.7	49.1
	δν	0	14.78	35.4	59.0	77.4	92.9	102.2	137.4	159.5	175.0	196.5	206.9
Colloidal Fe_2O_3	λ in X.U.	1737.2	1732.7	1726.6	1721.4	1719.6	1717.7	1714.7	1703.6	1696.0	1691.8	1689.9	
	δλ	0	4.52	10.62	15.82	17.6	19.5	22.5	33.6	41.2	45.4	47.3	
	δν	0	18.5	43.7	65.2	72.7	80.7	93.3	140.2	172.6	190.7	198.9	

TABLE II

Positions and Widths of Principal Absorption Edge in Solid and Colloidal Fe_2O_3

	λ in X.U.	ν/R	δλ	δν	Width in X.U.	Width in *e.v.*
Solid	1736.4	524.8	0	0	3.6	14.7
Colloidal	1737.2	524.6	.8	3.3	5.6	22.9

DISCUSSION

Secondary structures extending over several hundred volts may be either due to the crystal lattice or due to the polyatomic molecules. But the secondary structure from the crystalline field is different from that which simply arises from the molecular field. Further as the particle size diminishes its crystalline property may be different from that in which the particle size is large. Hence the secondary structures may also be different owing to the diminution of the particle size.

Our experimental results on colloidal solutions indicate that the secondary structure obtained in the colloidal solutions is different from that obtained in the solid Fe_2O_3. This difference in secondary structure suggests that if the colloidal particles exist in the crystalline state, their crystalline property is different from that in which it exists in the solid Fe_2O_3. This may be due to the diminution of particle size and as such there may be a change in the secondary structure. From the diffraction experiments on colloidal precipitates done in this laboratory,

we have observed that precipitates of metal sols are crystalline while non-conducting colloidal precipitates show amorphous bands coinciding in position with the strongest groups of sharp lines of the crystalline sample. This observation further complicates the problem as these diffraction bands (amorphous) may really arise from very small crystalline particles where the number of lattice planes is too small to show any perfect interference. Further the colloidal particles may also exist as simple molecular aggregation without any crystalline field. This may also account for a change in the secondary structure. At present it is however difficult to arrive at any definite conclusion as regards the two hypotheses, *viz*, whether the colloidal particles are simple molecular aggregation or small crystallites of Fe_2O_3.

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